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(56) Documents cited
GB 1425850 A GB 1339318 A GB 0728585 A
GB 0424564 A GB 0404571 A GB 0282738 A
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(54) Method of desulfurizing fuel oil

(57) A method of chemically desulfurizing fuel oil comprises the steps of: treating fuel oil with an oxidizing agent to oxidize an organic sulfur compound, eg a thiophene contained in the fuel oil into a sulfur oxide having heightened boiling and melting points and a different solubility based on the molecular polarity; and separating and removing the oxidised organic sulfur compound from the fuel oil through the utilization of the change in the boiling point, melting point and/or solubility of the organic sulfur compound. The separation/removal step may involve distillation and/or adsorption and/or precipitation and/or solvent extraction.

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METHOD OF DESULFURIZING FUEL OIL

The present invention relates to a method of chemically desulfurizing fuel oil by which a sulfur component contained in the fuel oil can be removed in an effective, economical and simple manner.

In general, fuel oil, that is, an oil derived from petroleum and coal, contains organic sulfur compounds. Since these organic sulfur compounds have chemical and physical properties similar to those of the fuel oil per se, it is very difficult to remove these sulfur compounds by separating means such as distillation. In order to solve this problem, development has hitherto been made on a method wherein fuel oil is reduced in the presence of a catalyst at high temperature under high pressure through the use of hydrogen to remove organic sulfur compounds contained in the fuel oil through the conversion of the organic sulfur compounds into hydrogen sulfide,

etc.

Further, there is a technique for removing sulfur through the oxidative decomposition of sulfur-containing hydrocarbon oil with an oxidizing agent. Specifically, Japanese Patent Laid-Open No. 45103/1974 disclosed a method wherein heavy oil is oxidatively decomposed in liquid phase to give a product having a low metal content. Japanese Patent Laid-Open No. 112609/1977 disclosed a desulfurization method which comprises treating sulfur-containing hydrocarbon oil with an oxidizing agent, adding an alkaline substance to the treated oil and heat-treating the mixture. Japanese Patent Laid-Open No. 290793/1987 disclosed a method wherein hydrocarbon oil is brought into contact with ozone to remove sulfur as sulfur dioxide.

Further, Japanese Patent Laid-Open No. 52803/1974 disclosed a technique wherein hydrocarbon oil is oxidized in the presence of a catalyst. Specifically, in this method, a sulfur-containing hydrocarbon substance is treated with an oxidizing agent and a molybdenum metal catalyst in the presence of an alcohol to reduce the sulfur content.

Japanese Patent Laid-Open No. 250092/1987 disclosed a technique for improving the quality of diesel oil which comprises reacting diesel oil with an

oxidizing agent and separating the treated oil by extraction.

In hydrodesulfurization widely used in the art on a commercial scale, use is made of a hydrogen gas at high temperature under high pressure in the presence of a metal catalyst such as cobalt, nickel, molybdenum or tungsten. Since, however, the reaction is conducted under vigorous conditions, this method has various technical and economic problems from the viewpoint of practical use, such as necessity for using a complicate and expensive apparatus and periodically regenerating a catalyst damaged by the action of a sulfur compound as a catalyst poison.

In the technique disclosed in the Japanese Patent Laid-Open No. 45103/1974, heavy oil is oxidatively decomposed in liquid phase and evaporated gas is cooled to separate it into a liquid product and gaseous hydrogen sulfide and sulfur dioxide. Since the liquid product is once gasified and then cooled, the yield of the liquid product based on the heavy oil is low disadvantageously.

In the technique disclosed in the Japanese Patent Laid-Open No. 112609/1977, sulfur-containing hydrocarbon oil is treated with an oxidizing agent and heat treated after an alkaline substance is added

thereto, and the resultant alkali sulfide and alkali salt of a sulfur oxide are removed. This method is disadvantageous in that it is necessary to provide the step of adding an alkaline substance and that the alkaline substance should be added in a sufficient amount.

In the technique disclosed in the Japanese Patent Laid-Open No. 290793/1977, hydrocarbon oil is brought into contact with ozone to remove sulfur as sulfur dioxide. This method is disadvantageous in that it is necessary to use an apparatus for recovering harmful sulfur dioxide and the percentage removal of sulfur is not very high.

In the technique disclosed in the Japanese Patent Laid-Open No. 52803/1974, a sulfur-containing hydrocarbon substance is treated with an oxidizing agent and a molybdenum metal catalyst in the presence of an alcohol. This method is disadvantageous in that the production cost is high because it is necessary to use a molybdenum metal catalyst in addition to an oxidizing agent.

Further, in the technique disclosed in the Japanese Patent Laid-Open No. 250092/1987, diesel oil is reacted with an oxidizing agent and the treated oil is separated by extraction. This method is

disadvantageous in that the step of extractive separation is complicate.

In order to solve the above-described problems, the present invention provides a method of chemically desulfurizing fuel oil, comprising the steps of: treating fuel oil with an oxidizing agent; oxidizing an organic sulfur compound contained in the fuel oil into a sulfur oxide having heightened boiling point and melting point and a different solubility based on the molecular polarity; and separating and removing the organic sulfur compound from the fuel oil through the utilization of the change in the boiling point, melting point and solubility of the organic sulfur compound.

Further, the present invention is characterized in that the fuel oil is selected from among naphtha (b.p.: 30°C or below), gasoline (b.p.: 30 to 220°C), kerosine (b.p.: 220 to 300°C), gas oil (b.p.: 300 to 360°C), heavy fuel oil, and crude oil.

Further, the present invention is characterized in that the oxidizing agent is selected from among oxygen gas, air, ozone gas, chlorine gas, hydrogen peroxide, peracetic acid, a mixture of aqueous hydrogen peroxide with an acid, performic acid, a

mixture of aqueous hydrogen peroxide with formic acid, perbenzoic acid, a mixture of aqueous hydrogen peroxide with benzoic acid, peroxychloroacetic acid, a mixture of aqueous hydrogen peroxide with chloroacetic acid, peroxydichloroacetic acid, a mixture of aqueous hydrogen peroxide with dichloroacetic acid, peroxytrichloroacetic acid, a mixture of aqueous hydrogen peroxide with trichloroacetic acid, peroxytrifluoroacetic acid, a mixture of aqueous hydrogen peroxide with trifluoroacetic acid, peroxymethanesulfonic acid, a mixture of aqueous hydrogen peroxide with methanesulfonic acid, hypochlorous acid and an aqueous hypochlorite solution.

Further, the present invention is characterized by reacting fuel oil with a peracid oxidizing agent or a hypochlorous acid oxidizing agent at a temperature in the range of from 0 to 140°C while agitating, separating an oil phase from the reaction mixture after the reaction, adding an aqueous alkaline solution to the oil to wash the oil, washing the oil further with water, drying the washed oil, and separating the resultant sulfur oxide from the oil.

Further, the present invention is characterized by reacting fuel oil with a gaseous oxidizing agent at

a temperature in the range of -20 to 50°C in such a manner that the gaseous oxidizing agent is bubbled through the reaction system, adding a reducing agent to the reaction mixture for washing, washing the oil further with water, drying the washed oil, and separating the resultant sulfur oxide from the oil.

Further, the present invention is characterized by reacting fuel oil with a gaseous oxidizing agent at a temperature in the range of -20 to 50°C in the presence of a photosensitizer in such a manner that the gaseous oxidizing agent is bubbled through the reaction system while irradiating the reaction system with light, adding a reducing agent to the reaction mixture for washing, washing the oil further with water, drying the washed oil, and separating the resultant sulfur oxide from the oil.

Further, the present invention is characterized by treating fuel oil with an oxidizing agent and distilling the treated fuel oil in the boiling point range of the fuel oil before the treatment through the use of a rectifier to separate an organic sulfur compound as a distillation residue.

Further, the present invention is characterized by treating fuel oil with an oxidizing agent, distilling the treated fuel oil in the boiling point

range of the fuel oil before the treatment through the use of a rectifier, and passing the resultant distillate through a column packed with an adsorbant selected from among activated carbon, silica gel and alumina or a combination of two or more of them to adsorb a sulfur component.

Further, the present invention is characterized by treating fuel oil with an oxidizing agent, cooling the treated fuel oil to such a temperature that insoluble components precipitate, allowing the cooled fuel oil to stand, separating an oil component by means of a filter or a separator, and distilling the oil component in the boiling point range of the fuel oil before the treatment through the use of a rectifier to separate an organic sulfur compound as a low-temperature insoluble and a distillation residue.

Further, the present invention is characterized by treating fuel oil with an oxidizing agent, cooling the treated fuel oil to such a temperature that insoluble components precipitate, allowing the cooled fuel oil to stand, separating an oil component by means of a filter or a separator, distilling the oil component in the boiling point range of the fuel oil before the treatment through the use of a rectifier, and passing the resultant distillate through a column

packed with an adsorbant selected from among activated carbon, silica gel and alumina or a combination of two or more of them to adsorb a sulfur component remaining in the distillate, thereby refining the fuel oil.

Although organic sulfur compounds contained in fuel oil are classified into many types and complicate, it is known that they are mainly chemically stable thiophene compounds having a divalent sulfur atom.

The present invention is based on the fact that physical and chemical properties inherent in an organic sulfur compound, that is, the boiling point, melting point, solubility in an organic solvent and other properties, undergo a remarkable change depending upon its state of oxidation, that is, when a divalent sulfur atom is bonded to an oxygen atom by oxidation to yield a sulfoxide, a sulfone and a sulfonic acid containing a sulfur atom having a higher valency.

Accordingly, the present invention is characterized by oxidizing an organic sulfur compound contained in fuel oil into a corresponding compound, such as a sulfoxide, a sulfone or a sulfonic acid through the use of an oxidizing agent commercially

available at a low cost, such as oxygen gas or air, ozone, hydrogen peroxide, peracid or hypochlorous acid, and simply and effectively removing the sulfur component by the conventional refining method, such as distillation, extraction with a solvent, low-temperature separation or column chromatography through the utilization of a remarkable rise in the boiling point and melting point and a difference in the solubility based on the molecular polarity caused by the above-described conversion.

The fuel oil to be used in the present invention may be any of petroleum and liquefied coal oil, that is, crude oil, natural asphalt or bitumen and their distillation fraction, topped crude, vacuum residue, pitchy material obtained from the residue, gasoline, kerosine, gas oil, heavy oil, shale oil, liquefied coal, etc. They may be used in the oxidation as such or in the form of a mixture with other organic solvent.

The oxidizing agent to be used in the present invention may be a reagent commonly used in the oxidation of an organic sulfur compound, and examples thereof include oxygen gas, air, ozone, chlorine gas, hydrogen peroxide, peracetic acid, a mixture of aqueous hydrogen peroxide with an acid, performic

acid, a mixture of aqueous hydrogen peroxide with formic acid, perbenzoic acid, a mixture of aqueous hydrogen peroxide with benzoic acid, peroxychloroacetic acid, a mixture of aqueous hydrogen peroxide with chloroacetic acid, peroxydichloroacetic acid, a mixture of aqueous hydrogen peroxide with dichloroacetic acid, peroxytrichloroacetic acid, a mixture of aqueous hydrogen peroxide with trichloroacetic acid, peroxytrifluoroacetic acid, a mixture of aqueous hydrogen peroxide with trifluoroacetic acid, peroxymethanesulfonic acid, a mixture of aqueous hydrogen peroxide with methanesulfonic acid, hypochlorous acid and an aqueous hypochlorite solution.

The oxidation method may be any of a method wherein the fuel oil is used as a reaction solvent as such and a method wherein a mixed solvent comprising the fuel oil and various organic solvents is used for the purpose of increasing the solubility of the oxidizing agent in the fuel oil. For example, in an oxidization reaction wherein oxygen is used as an oxidizing agent, use is made of singlet oxygen formed by irradiation with a tungsten lamp in the presence of a photosensitizer. A direct oxidation reaction wherein use is made of ozone may also be used

according to the conventional method. In the reaction with an organic peracid or a mixture of hydrogen peroxide with various acids, the system often becomes heterogeneous since the organic peracid and the mixtures are hardly soluble in the fuel oil, so that the conversion generally lowers. In this case, it is possible to remarkably improve the conversion by a method wherein a solvent capable of remarkably improving the mutual solubility, such as acetone, is added, or a method wherein the reaction is conducted while forcibly dispersing and agitating the reaction solution by mechanical means or by means of an ultrasonic homogenizer.

The reaction in the present invention is conducted under atmospheric pressure at a temperature in the range of from 0 to 200°C. When the reaction is conducted in an aqueous caustic alkali solution in the presence of oxygen gas, the pressure and the reaction temperature are 1 to 30 atm, preferably 15 atm, and 250 to 400°C, respectively. On the other hand, when the reaction is conducted in an aqueous caustic alkali solution in the presence of oxygen gas, the pressure and the reaction temperature are 1 to 30 atm, preferably 15 atm, and 250 to 400°C, preferably 370°C, respectively.

In general, the removal of a sulfur component from the fuel oil according to the present invention can be simply conducted by a distillation procedure through the utilization of the rise of the boiling point of an organic sulfur compound formed by the oxidation. Further, techniques wherein use is made of a change in the solubility and melting point, such as extraction with a solvent, low-temperature separation and column chromatography, may be used alone or in a combination of two or more of them.

FUNCTION

In the above-described method of chemically desulfurizing fuel oil to remove a sulfur component contained therein, the sulfur content of gasoline, kerosine, gas oil and heavy oil can be reduced to 0.03% or less. The mechanism of function of the present invention is based on the fact that physical and chemical properties inherent in an organic sulfur compound, that is, the boiling point, melting point, solubility in an organic solvent and other properties, undergo a remarkable change depending upon its state of oxidation. For example, the boiling point of dimethyl sulfide is 38°C under atmospheric pressure, while the boiling point of dimethyl sulfoxide formed by the oxidation of dimethyl sulfide is 189°C.

Further, dimethyl sulfone formed by the oxidation of dimethyl sulfide is in a state of crystal having a melting point of 110°C under atmospheric pressure which is difficult to distill. It is known that all of these oxidation products have a larger polarity than those of the corresponding dimethyl sulfide, which causes the solubility in an organic solvent to be remarkably changed.

[Examples]

The present invention will now be described with reference to the following Examples.

Example 1

50 ml of a fuel oil (combustible sulfur content: 0.063% by weight) obtained by frictional distillation in a boiling temperature range of from 220 to 300°C was cooled to 0°C in a 200-ml round-bottomed hard glass flask equipped with a homogenizer agitator, a reflux condenser and a gas introduction tube, and agitation was conducted for 2 hr while blowing air containing ozone (about 1.0%) into the fuel oil. After the supply of ozone was stopped, the temperature of the whole flask was lowered to -20°C and agitation was continued for additional one hr. Then the precipitated solid matter was quickly separated by filtration. The filtrate was washed with a 2 N

aqueous sodium sulfite solution and further with distilled water, and the resultant organic phase was distilled by means of a rectifier to collect fractions having boiling points in the range of from 220 to 300°C. The total sulfur content in the resultant refined oil was 0.022%.

Example 2

A 200-ml round-bottomed hard glass flask equipped with a homogenizer agitator, a reflux condenser and a gas introduction tube was charged with added 50 ml of a fuel oil (combustible sulfur content: 0.023% by weight) obtained by fractional distillation in a boiling temperature range of from 70 to 220°C, 20 ml of methanol and 0.15 g of a photosensitizer (Rose Bengal), and the mixture was irradiated with a 300-W halogen lamp at room temperature for 6 hr while blowing oxygen gas into the mixture. After the reaction, the reaction mixture was washed with a 2 N aqueous sodium sulfite solution and further with distilled water, and distilled by means of a rectifier. The total sulfur content in the resultant fractions having boiling points in the range of from 70 to 220°C was 0.012%.

Example 3

50 ml of a fuel oil (combustible sulfur content:

0.527% by weight) obtained by fractional distillation in a boiling temperature range of from 300 to 360°C was put in a 200-ml round-bottomed hard glass flask equipped with a homogenizer agitator and a reflux condenser, and 5 ml of aqueous hydrogen peroxide (30%) and 10 ml of formic acid were added thereto. After, a reaction was allowed to proceed while agitating the mixture at 40°C for 1 hr and then at 80°C for 2 hr, an upper layer of the reaction mixture separated into two layers was separated by means of a separatory funnel, washed with a 2 N aqueous sodium sulfite solution and further with distilled water, and the resultant organic phase was distilled by means of a rectifier to collect fractions having boiling points in the range of from 220 to 350°C. The total sulfur content in the refined oil was 0.043%. This oil was passed through a glass column packed with 20 g of alumina to give a refined oil having a total sulfur content of 0.011%.

Example 4

50 ml of a fuel oil (combustible sulfur content: 0.527% by weight) obtained by fractional distillation in a boiling temperature range of from 300 to 360°C was put in a 200-ml round-bottomed hard glass flask equipped with a homogenizer agitator and a reflux condenser, and 5 ml of aqueous hydrogen peroxide (30%)

and 10 ml of dichloroacetic acid were added thereto. After a reaction was allowed to proceed while agitating the mixture at 40°C for 3 hr, an upper layer of the reaction mixture separated into two layers was separated by means of a separatory funnel and washed with a 2 N aqueous sodium sulfite solution and further with distilled water, and the resultant organic phase was distilled by means of a rectifier to collect fractions having boiling points in the range of from 300 to 360°C. The total sulfur content in the refined oil was 0.022%. This oil was passed through a glass column packed with 20 g of silica gel to give a refined oil having a total sulfur content of 0.008%.

Example 5

50 ml of a fuel oil (combustible sulfur content: 0.023% by weight) obtained by fractional distillation in a boiling temperature range of from 70 to 220°C and 10 ml of distilled water were put in a 200-ml round-bottomed hard glass flask equipped with a homogenizer agitator, a reflux condenser and a gas introduction tube, and a reaction was allowed to proceed at 0°C for one hr with agitation while blowing chlorine gas into the mixture. After the reaction, the resultant organic phase was separated and washed with a 2 N aqueous sodium sulfite solution, and the resultant

organic phase was distilled by means of a rectifier. The total sulfur content in the fractions having boiling points in the range of from 70 to 220°C was 0.007%.

Example 6

50 ml of a fuel oil (combustible sulfur content: 0.527% by weight) obtained by fractional distillation in a boiling temperature range of from 300 to 360°C was put in a 200-ml round-bottomed hard glass flask equipped with a homogenizer agitator and a reflux condenser, and 20 ml of an aqueous sodium hyposulfite solution (Cl: 5%) was added thereto. After a reaction was allowed to proceed at 30°C for 3 hr while agitating, an upper layer of the reaction mixture separated into two layers was separated by means of a separatory funnel, washed with a 2 N aqueous sodium sulfite solution and further with distilled water, and the resultant organic phase was distilled by means of a rectifier to collect fractions having boiling points in the range of from 300 to 360°C. The total sulfur content in the refined oil was 0.108%.

Example 7

50 ml of a commercially available heavy oil A (combustible sulfur content: 0.833% by weight) was put in a 200-ml round-bottomed hard glass flask equipped

with a homogenizer agitator and a reflux condenser, and 5 ml of aqueous hydrogen peroxide (30%) and 10 ml of trifluoroacetic acid were added thereto. After a reaction was allowed to proceed at 20°C for one hr while agitating, an upper layer of the resultant reaction mixture separated into two layers was separated by means of a separatory funnel and washed with a 2 N aqueous sodium sulfite solution and further with distilled water. 100 ml of petroleum ether (b.p.: 35 to 60°C) was added thereto and the mixture was cooled to -40°C and allowed to stand for 2 hr. An upper layer of the mixture separated into two layers was separated, dried and passed through a glass column packed with 10 g of alumina and 10 g of silica gel in two layers. The petroleum ether was removed from the resultant oil by distillation. The total sulfur content in the residue was 0.145%.

Example 8

50 ml of a fuel oil (combustible sulfur content: 0.527% by weight) obtained by fractional distillation in a boiling temperature range of from 300 to 360°C was put in a 200-ml round-bottomed hard glass flask equipped with a homogenizer agitator and a reflux condenser, and 5 ml of aqueous hydrogen peroxide (30%) and 10 ml of trifluoroacetic acid were added thereto.

After a reaction was allowed to proceed at 20°C for one hr while agitating, an upper layer of the resultant reaction mixture separated into two layers was separated by means of a separatory funnel and washed with a 2 N aqueous sodium sulfite solution and further with distilled water. The resultant organic phase was distilled by means of a rectifier to collect fractions having boiling points in the range of from 300 to 360, which were passed through a glass column packed with 10 g of alumina and 10 g of silica gel in two layers. The total sulfur content in the refined oil was 0.005%

CLAIMS:

(1) A method of chemically desulfurizing fuel oil, comprising the steps of: treating fuel oil with an oxidizing agent; oxidizing an organic sulfur compound contained in the fuel oil into a sulfur oxide having heightened boiling point and melting point and a different solubility based on the molecular polarity; and separating and removing the organic sulfur compound from the fuel oil through the utilization of the change in the boiling point, melting point and solubility of the organic sulfur compound.

(2) A method of chemically desulfurizing fuel oil according to claim 1, wherein the fuel oil is selected from among naphtha (b.p.: 30°C or below), gasoline (b.p.: 30 to 220°C), kerosine (b.p.: 220 to 300°C), gas oil (b.p.: 300 to 360°C), heavy fuel oil, and crude oil.

(3) A method of chemically desulfurizing fuel oil according to claim 1, wherein the oxidizing agent is selected from among oxygen gas, air, ozone gas, chlorine gas, hydrogen peroxide, peracetic acid, a mixture of aqueous hydrogen peroxide with an acid, performic acid, a mixture of aqueous hydrogen peroxide with formic acid, perbenzoic acid, a mixture of

the range of from 0 to 140°C while agitating, separating an oil phase from the reaction mixture after the reaction, adding an aqueous alkaline solution to the oil to wash the oil, washing the oil further with water, drying the washed oil, and separating the resultant sulfur oxide from the oil.

(6) A method of chemically desulfurizing fuel oil according to claim 1, which comprises reacting fuel oil with a gaseous oxidizing agent at a temperature in the range of from -20 to 50°C in such a manner that the gaseous oxidizing agent is bubbled through the reaction system, adding a reducing agent to the reaction mixture for washing, washing the oil further with water, drying the washed oil, and separating the resultant sulfur oxide from the oil.

(7) A method of chemically desulfurizing a fuel oil according to claim 1, which comprises reacting a fuel oil with a gaseous oxidizing agent at a temperature in the range of from -20 to 50°C in the presence of a photosensitizer in such a manner that the gaseous oxidizing agent is bubbled through the reaction system while irradiating the reaction system with light, adding a reducing agent to the reaction mixture for washing, washing the oil further with water, drying the washed oil, and separating the

resultant sulfur oxide from the oil.

(8) A method of chemically desulfurizing fuel oil according to claim 1, which comprises treating fuel oil with an oxidizing agent and distilling the treated fuel oil in the boiling point range of the fuel oil before the treatment through the use of a rectifier to separate an organic sulfur compound as a distillation residue.

(9) A method of chemically desulfurizing fuel oil according to claim 1, which comprises treating fuel oil with an oxidizing agent, distilling the treated fuel oil in the boiling point range of the fuel oil before the treatment through the use of a rectifier, and passing the resultant distillate through a column packed with an adsorbant selected from among activated carbon, silica gel and alumina or a combination of two or more of the adsorbents to adsorb a sulfur component.

(10) A method of chemically desulfurizing fuel oil according to claim 1, which comprises treating fuel oil with an oxidizing agent, cooling the treated fuel oil to such a temperature that insoluble components precipitate, allowing the cooled fuel oil to stand, separating an oil component by means of a filter or a separator, and distilling the oil

component in the boiling point range of the fuel oil before the treatment through the use of a rectifier to separate an organic sulfur compound as a low-temperature insoluble and a distillation residue.

(11) A method of chemically desulfurizing fuel oil according to claim 1, which comprises treating a fuel oil with an oxidizing agent, cooling the treated fuel oil to such a temperature that insoluble components precipitate, allowing the cooled fuel oil to stand, separating an oil component by means of a filter or a separator, distilling the oil component in the boiling point range of the fuel oil before the treatment through the use of a rectifier, and passing the resultant distillate through a column packed with an adsorbant selected from among activated carbon, silica gel and alumina or a combination of two or more of the adsorbents to adsorb a sulfur component remaining in the distillate, thereby refining the fuel oil.

(12) A method of chemically desulfurizing fuel oil according to claim 1, wherein the organic sulfur compound contained in the fuel oil is a chemically stable thiophene compound having a divalent sulfur atom, and the divalent sulfur atom of the thiophene compound is combined with oxygen by oxidation to

convert the thiophene compound into a sulfoxide, a sulfone and a sulfonic acid containing a sulfur atom having a higher valency.

13. A method of chemically desulfurizing fuel oil substantially as hereinbefore described in the Examples.

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Examiner's report to the Comptroller under
Section 17 (The Search Report)

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Relevant Technical fields

(i) UK CI (Edition L) C5E (ETA, ETB, ETC)

(ii) Int CI (Edition 5) C10G

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES: WPI, CLAIMS

Search Examiner

R J WALKER

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9 MARCH 1993

Documents considered relevant following a search in respect of claims 1-12

Category (see over)	Identity of document and relevant passages		Relevant to claim(s)
X	GB 1425850	(ATLANTIC RICHFIELD CO) page 2 lines 23-46, page 5 lines 52-89	At least Claims 1, 2,3,12
X	GB 1339318	(INSTITUT NEFTEKHIMICHESKOGO ETC) - page 2 lines 25-49	At least Claims 1, 2,3
X	GB 728585	(THE BRITISH PETROLEUM CO LTD) - page 1 lines 75-91	At least Claims 1, 2,3,8,9
X	GB 424564	(HERZENBERG) - Example 1	At least Claims 1, 2,3,8
X	GB 404571	(BOULANSER) - page 1 line 55 - page 2 line 16	At least Claims 1, 2,3
X	GB 282738	(AXTELL RESEARCH LABORATORIES)	At least Claims 1, 2,8,10
X	US 3960683	(BABA)	At least Claims 1, 2,3,6,7

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

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